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Isostructural cobalt(II) and zinc(II) complexes of the *N*,*N*-bis(carboxymethyl)-β-alaninato(3−) ion. Crystal structure of the cobalt(II) derivative, $[Co(H_2O)_6][Co_2L_2(H_2O)_2]\cdot4H_2O$

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Abstract

Homonuclear compounds $[M(H_2O)_6[M_2L_2(H_2O)_2]\cdot4H_2O$ (M(II) = Co(II) or Zn(II), L^{3-} = anion of *N*,*N*-bis(carboxymethyl)-β-alanine or ((2-carboxyethyl)imino)diacetic acid) have been synthesized and characterized by chemical analysis, magnetic susceptibility data and/or IR spectra, thermal analysis and X-ray diffraction method. They are isostructural and crystallize in the triclinic system, space group $P\bar{1}$ with $Z = 1$. The crystal structure was determined for the cobalt(II) compound ($a = 8.732(7)$, $b = 9.751(6)$, $c = 9.918(5)$ Å, $\alpha = 99.96(4)$, $\beta = 110.88(5)$, $\gamma = 103.79(5)°$, $V = 734.6$ Å^3, $D_{meas} = 1.80$ g cm^{-3}, $D_{exp} = 1.80$ g cm^{-3}, $\mu = 1.767$ mm^{-1} (MoKα)). Final $R = 0.034$ and $R_w = 0.043$ for 3145 independent observed reflections. This compound consists of both centrosymmetric hexaaquocobalt(II) cations (Co(1)–OW(1) = 2.046(2), Co(1)–OW(2) = 2.077(2), Co(1)–OW(3) = 2.119(2) Å) and anions $[Co_2L_2(H_2O)_2]^{2-}$, and non-coordinated water molecules. In the homodinuclear chelate anions, each cobalt(II) atom is bonded to one water molecule (Co(2)–OW(4) = 2.098(2) Å) and one tetradentate chelating ligand L^{3-} (Co(2)–N = 2.134(2), Co(2)–O(5) = 2.113(2), Co(2)–O(13) = 2.081(2), Co(2)–O(23) = 2.101(2) Å). The dimer has an imposed C_i symmetry. One carboxylate oxygen atom from the β-alanine arm acts as a bridge between the two cobalt atoms so completing the octahedral coordination of cobalt. The values of the distances Co(2)–Co(2^i) and the angle at the oxygen atom Co(2)–O(5)–Co(2^i) are 3.2934(7) Å and 103.5(1)°, respectively.

Introduction

The structural studies of metal chelates of amino acids and aminopolycarboxylic acids show examples where their carboxyl functions (carboxylic and/or carboxylate groups) play a variety of roles. In addition to 'free' and metal-bonded carboxylic groups (in 'acid' metal chelates), 'free' mono-, bi- and tri-dentate carboxylate groups are known in such metal chelate compounds. The tridentate role is very unusual and it arises when one of the oxygen atoms is bonded to a metal ion and both oxygen atoms of the same carboxylate group are bonded to a second metal ion (so that an irregular four-membered chelate ring results) [1–3]. Some examples are known in which a side-chain or terminal carboxylate group has both oxygen atoms bonded to the same metal in an unsymmetrical chelate ring [4, 6] whereas the for-

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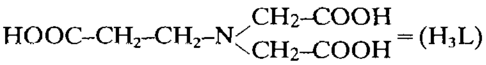
mation of M–O–C–O–M bridges is a common way to yield extended polynuclear structures in the referred metal chelates [1, 2, 4].

In a previous paper, we reported the crystal structure and other results about a copper(II) derivative of the *N,N*-bis(carboxymethyl)-*β*-alanine or ((2-carboxyethyl)imino)diacetic acid (H_3L), with an unusual six-membered *β*-aminopropionic acid–copper(II) chelate ring [5].



$$HOOC\text{–}CH_2\text{–}CH_2\text{–}N\begin{array}{l}\diagup CH_2\text{–}COOH\\ \diagdown CH_2\text{–}COOH\end{array} = (H_3L)$$

Attempts to obtain suitable crystals of other $(MHL)\cdot nH_2O$ compounds [6] for structural X-ray diffraction studies have been carried out. In this way, when using polycrystalline samples of $Co(HL)\cdot nH_2O$ as a 'starting' material, well formed crystals of a 'non-acid' cobalt(II) derivative of H_3L were obtained. The synthesis of this unexpected Co(II) compound was then restated and attempted for other divalent transition metal ions. This paper reports the synthesis and characterization of the new cobalt(II) and zinc(II) homonuclear compounds.

Experimental

Ligand synthesis

N,N-Bis(carboxymethyl)-*β*-alanine or ((2-carboxyethyl)imino)diacetic acid (H_3L), was prepared by the method [7] used earlier [5].

Synthesis of complexes

Hexaaquacobalt(II)bis(μ-β-alaninato-N,N-diacetato)diaquadicobaltate(II) tetrahydrate

This compound is obtained in aqueous medium by reaction of stoichiometric amounts of ((2-carboxyethyl)imino)diacetic acid (H_3L) and cobalt hydroxycarbonate in a molar ratio of 4:3. For example, to 12.19 mmol of H_3L in 150 ml of water was slowly added 9.14 mmol of $Co_2CO_3(OH)_2\cdot 2H_2O$. The reaction mixture was heated ($T = 80$ °C) and gently stirred under vacuum (to remove the CO_2 by-product). The clear pink solution was slowly cooled to room temperature, filtered and allowed to evaporate for several days. The dark pink crystals formed were filtered and washed with cool water, ethanol and acetone, and then air-dried. If necessary, the compound can be recrystallized from hot water. Yield: $\geqslant 70\%$. The last fraction of mother liquor precipitates a crude pink material (with or without the appearance of white free H_3L). This starting material can be purified by recrystallization from excess hot water, thus yielding separately dark pink crystals of the desired product and white crystals of H_3L. *Anal.* Calc. for $C_{14}H_{40}Co_3N_2O_{24}$: C, 21.09; H, 5.06; N, 3.51; Co, 22.16. Found: C, 21.2; H, 5.1; N, 3.5; Co, 22.5%.

Hexaaquazinc(II)bis(μ-β-alaninato-N,N-diacetato)diaquadizincate(II) tetrahydrate

This compound was prepared by a procedure analogous to that of the cobalt(II) solid, by reacting H_3L and $2ZnCO_3\cdot 3Zn(OH)_2$ in the molar ratio 10:3. The white parallelepiped crystals of this compound and the needle crystals of the ligand acid form (H_3L) are readily distinguishable and eventually can easily be removed. The yield is usually very high: 90%. *Anal.* Calc. for $C_{14}H_{40}N_2O_{24}Zn_3$: C, 20.59; H, 4.94; N, 3.43; Zn, 24.02. Found: C, 21.1; H, 4.9; N, 3.5; Zn, $23 \pm 1\%$.

By reaction of the appropriate amounts of H_3L and metal(II) hydroxycarbonate (M = Cu, Ni, Co, Zn) in the acid-to-metal molar ratio 1:1, it should be possible to obtain solid samples of the compounds $M(HL)\cdot nH_2O$. The crystal structure of $[Cu(HL)\cdot(H_2O)]$ has been solved by the X-ray diffraction method [5]. However, the recrystallizations of compounds $M(HL)\cdot nH_2O$ with M = Co and Zn require considerable amounts of hot water, and the precipitation of the resulting dilute aqueous solutions occurs with disproportionation to $[M(H_2O)_6]$-$[M_2L_2(H_2O)_2]\cdot 4H_2O$ and H_3L in the molar ratio 1:1, by the reaction

$$3M(HL)\cdot nH_2O \text{ (in water)} \longrightarrow [M(H_2O)_6][M_2L_2(H_2O)_2]\cdot 4H_2O + H_3L$$

X-ray structure determination

Diffraction data for $[Co(H_2O)_6][Co_2L_2(H_2O)_2]\cdot 4H_2O$ were collected at room temperature on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The pink single crystals were shaped as parallelepipeds with dimensions $0.30 \times 0.20 \times 0.19$ μm. Details of crystal data, intensity collection and refinement are reported in Table 1. Lattice constants were obtained by a least-squares fit of 25 reflections in the range $4.63 < 2\theta < 21.91°$. The intensities of three standard reflections measured every 50 reflections showed no systematic variation. Absorption correction was not necessary. No extinction correction was performed. Direct methods [8] (MULTAN 80 and DIRDIF) were used to solve the structure, by locating the cobalt atoms and in a second step, carbon, nitrogen and oxygen atoms. The structure was refined by full-matrix least-squares methods [9] to final residuals $R_F = 0.034$ and $R_{wF} = 0.043$ with $w = 1/\sigma^2(F)$, minimizing the function $\Sigma_{hkl}w_{hkl}(|F_o| - |kF_c|)^2$. H atoms could be located from difference maps but were not

TABLE 1. Summary of crystal data, intensity collection and structure refinement

Formula	$Co_3C_{14}H_{40}N_2O_{24}$
M_r	797.23
Triclinic space group	$P\bar{1}$
a (Å)	8.732(7)
b (Å)	9.751(6)
c (Å)	9.918(5)
α (°)	99.96(4)
β (°)	110.88(5)
γ (°)	103.79(5)
V (Å^3)	734.6
Z	1
D_{meas} (g cm^{-3})	1.80(2)
D_{exp} 1.80 (g cm^{-3})	1.80
μ (Mo Kα)	1.767
Scan type	θ–2θ
Scan width	0.7° below Kα_1 and 0.7° above Kα_2
Scan range (°)	$1 < \theta < 32°5$
Octants collected	$-14 \leqslant h \leqslant 14$; $-15 \leqslant k \leqslant 15$; $0 \leqslant l \leqslant 15$
No. independent reflections measured	5348
Final R	0.034[a]
Final R_w	0.043[a]

[a] For 3145 independent observed reflections with $I > 4\sigma(I)$.

refined and were assigned isotropic thermal parameters 1 Å^2 higher than the isotropic factor of the corresponding C or N atom. Final atomic positional parameters and equivalent isotropic temperature are listed in Table 2. All calculations were performed with the local system of programs adapted for the UNIVAC 1110 computer [10].

Physical measurements

The TG and DTA diagrams, IR spectra and the magnetic susceptibility data were obtained as described in ref. 5 for the solid-state derivative [Cu(HL)(H_2O)] of *N*-(2-carboxyethyl)iminodiacetic acid.

TABLE 2. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.s in parentheses

	x	y	z	B_{eq} (Å^2)[a]
Co(1)	1.0	0.5	1.0	1.86
Co(2)	0.56909(4)	0.08386(4)	0.39189(4)	1.48
N	0.4752(3)	0.2260(2)	0.2664(2)	1.87
C(1)	0.3504(4)	0.2738(3)	0.3157(4)	2.44
C(2)	0.1914(4)	0.1504(4)	0.2924(4)	2.60
C(3)	0.2146(3)	0.0496(3)	0.3926(3)	1.80
O(4)	0.0842(3)	−0.0261(3)	0.3980(3)	2.99
O(5)	0.3686(2)	0.0480(2)	0.4668(2)	1.85
C(11)	0.6281(4)	0.3571(3)	0.3092(3)	2.20
C(12)	0.7442(4)	0.3961(3)	0.4768(3)	2.08
O(13)	0.7309(3)	0.2911(2)	0.5366(2)	2.52
O(14)	0.8447(3)	0.5234(2)	0.5418(2)	2.85
C(21)	0.3945(4)	0.1483(3)	0.1038(3)	2.31
C(22)	0.3352(4)	−0.0186(3)	0.0747(3)	2.03
O(23)	0.3912(3)	−0.0695(2)	0.1852(2)	2.27
O(24)	0.2388(3)	−0.0959(2)	−0.0555(2)	3.15
OW(1)	0.8558(3)	0.3112(2)	0.8268(2)	2.96
OW(2)	0.9732(3)	0.3860(2)	1.1533(2)	3.09
OW(3)	1.2203(3)	0.4431(3)	1.0025(3)	3.21
OW(4)	0.7633(3)	0.0642(3)	0.3196(3)	3.92
OW(5)	0.1479(3)	0.3149(3)	0.6817(3)	3.58
OW(6)	0.4827(4)	0.3223(3)	0.8418(4)	5.44

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\vec{a}_i \cdot \vec{a}_j$.

Results and discussion

Description of the structure

The unit cell of the reported Co(II) compound contains, on an average, one hexaaquacobalt(II) cation, one dimeric chelate anion $[Co_2L_2(H_2O)_2]^{2-}$ and four water molecules. An ORTEP drawing of the homodinuclear anion with the labeling scheme is given in Fig. 1. Bond lengths and angles are given in Table 3. See also 'Supplementary material'.

Cobalt(II) coordination polyhedra

The octahedral cation $[Co(H_2O)_6]^{2+}$ is slightly distorted, but centrosymmetric, with the atom Co(1) at the inversion center. Their average distance Co(1)–OW is 2.09(6) Å and the right angles (86.5–92.7(1)°) approach the ideal value of 90°. Analogous hexaaquacobalt(II) ions are previously reported in the crystal structures of several cobaltous salts, with remarkably different counter-anions [11–14]. In these examples, the average Co(II)–OW bond distance falls in the range of 2.08(6)–2.11(6) Å and their slightly distorted hexaaqua cations are often centrosymmetric [11, 13, 14]. The reported homodinuclear anion $[Co_2L_2(H_2O)_2]^{2-}$ has an imposed C_i symmetry. Each cobalt(II) atom is bonded to one water molecule OW(4) and chelated by one ligand L^{3-}, which acts as tetradentate via their donor atoms N, O(5), O(13) and O(23). In addition, one carboxylate oxygen atom $O(5^i)$ from the β-alaninato arm of the symmetry related ligand L^{3-} acts as a bridge between the two cobalt atoms, so completing the octahedral coordination of this chelated ion. In the environment of each cobalt atom, the four oxygen atoms O(5), O(13), O(23) and OW(4) define a distorted tetragonal mean plane P(2) from which the atoms O(13) and O(23) are moved ~0.28 Å towards the apical N atom and in the opposite sense, the atoms Co(2), O(5) and OW(4) deviate 0.14, 0.23 and 0.50 Å, respectively (see 'Supplementary material').

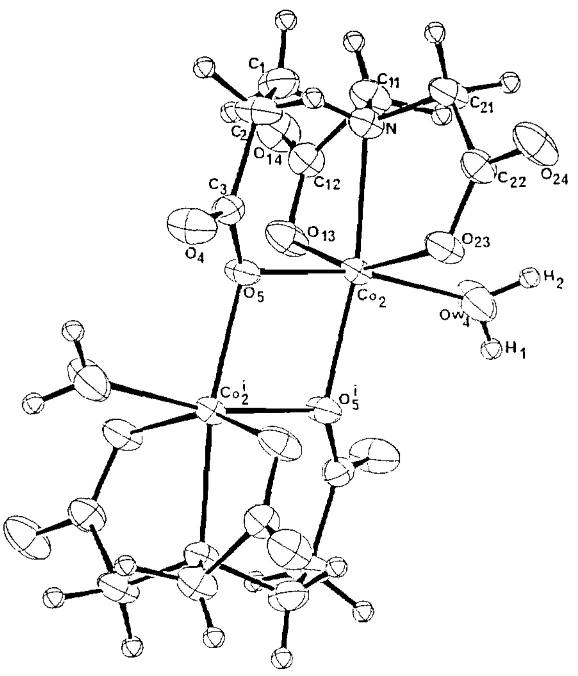


Fig. 1. ORTEP view of the anionic portion $[Co_2L_2(H_2O)]^-$ of the title compound.

Although, to our knowledge, no structural data of Co_2O_2 units with bridging monoatomic oxygen atoms of carboxylate groups are described, several copper(II) complexes have been reported with analogous Cu_2O_2 units built up with two monoatomic acetate bridging ligands [15–19]. In the Cu_2O_2 unit of these copper(II) derivatives, the Cu–Cu distance ranges from 3.30 to 3.51 Å, whereas the Cu–O–Cu angle is open from 95.3 to 102.5°.

Chelate rings and conformation of the ligand

In the dimeric anion $[Co_2L_2(H_2O)_2]^{2-}$, the aminotricarboxylate anions L^{3-} play a bridging role and act as tetradentate chelating agents. The chelation of each of these cobalt(II) atoms is made by formation of two five-membered and one six-membered chelate rings. This latter is a β-alaninato–cobalt(II) ring, which exhibits the usual boat-type conformation, also found in other β-aminopropionato–metal(II) complexes [4, 5, 20] and, among them, the isostructural $[M(\beta\text{-alaninato})_2(H_2O)_2]$ of Co(II) and Ni(II) [4, 20].

On the other hand, in the dimeric anion, both cobalt(II)–glycinate rings are distorted in asymmetric envelope conformations [20]. The cobalt(II) atom (with deviation < 0.005 Å) virtually lies in the mean planes, P(5) for Co(2), N, C(11), C(12) and O(13), and P(6) for Co(2), N, C(21), C(23) which form a dihedral angle of 167°4. Also the carboxylate oxygen atoms typically lie on either side of the mean planes of these rings (see 'Supplementary material'). In addition, the angles N–Co(II)–O of both five-membered rings agree reasonably well with the observed correlation of the N–M(II)–O angle in α-amino acid chelate rings versus the mean metal–ligand distances [4, 20].

The internal geometry of the ligand L^{3-} correlates well with the values reported in the literature concerning the bond lengths and angles [4]. For example, the torsion angles values Co(2)–N–C(1)–C(2) (−60.9(3)°), N–C(1)–C(2)–C(3) (71.6(4)°), C(1)–C(2)–C(3)–O(5) (−16.6(4)°), C(2)–C(3)–O(5)–Co(2)(−31.8(3)°), C(3)–O(5)–Co(2)–N (30.1(2)°) and O(5)–Co(2)–N–C(1) (15.8(2)°) of the six-membered chelate ring are close to the corresponding

TABLE 3. Bond lengths (Å) and angles (°)

Hexaaquacobalt(II) cation			
Co(1)-OW(1)	2.046(2) [2][a]	OW(1)-Co(1)-OW(2)	90.17(8)
Co(1)-OW(2)	2.077(2) [2]	OW(1)-Co(1)-OW(3)	86.5(1)
Co(1)-OW(3)	2.119(2) [2]	OW(2)-Co(1)-OW(3)	92.7(1)
Dinuclear anion: $[Co_2L_2(H_2O)_2]^{2-}$			
Co(2)-OW(4)	2.098(2)	Co(2)-O(23)	2.101(2)
Co(2)-N	2.134(2)	Co(2)-O(5^{i})[b]	2.080(2)
Co(2)-O(5)	2.113(2)	Co(2)...Co(2^{i})	3.2934(7)
Co(2)-O(13)	2.081(2)	Co(1)...Co(2)	5.9223(3)
OW(4)-Co(2)-O(13)	89.8(1)	O(13)-Co(2)-O(5)	100.55(8)
OW(4)-Co(2)-O(23)	86.8(1)	O(13)-Co(2)-O(5^{i})	100.68(8)
OW(4)-Co(2)-N	98.84(9)	O(23)-Co(2)-O(5^{i})	103.22(8)
O(13)-Co(2)-O(23)	155.93(8)	O(23)-Co(2)-O(5)	87.86(8)
O(13)-Co(2)-N	78.00(8)	N-Co(2)-O(5)	93.51(8)
O(23)-Co(2)-N	79.00(8)	N-Co(2)-O(5^{i})	169.57(8)
OW(4)-Co(2)-O(5)	165.3(1)	O(5)-Co(2)-O(5^{i})	76.49(8)
OW(4)-Co(2)-O(5^{i})	91.48(8)		
Ligand: L^{2-}			
N-C(1)	1.479(4)	C(11)-C(12)	1.527(4)
N-C(11)	1.480(3)	C(12)-O(13)	1.271(3)
N-C(21)	1.478(3)	C(12)-O(14)	1.236(3)
C(1)-C(2)	1.518(4)	C(21)-C(22)	1.526(4)
C(2)-C(3)	1.512(4)	C(22)-O(23)	1.268(3)
C(3)-O(4)	1.224(3)	C(22)-O(24)	1.237(3)
C(3)-O(5)	1.288(3)		
Co(2)-N-C(1)	108.9(2)	C(11)-C(12)-O(13)	115.9(2)
Co(2)-N-C(11)	105.6(2)	C(11)-C(12)-O(14)	118.5(2)
Co(2)-N-C(21)	109.6(2)	O(13)-C(12)-O(14)	125.6(3)
C(1)-N-C(11)	108.1(2)	N-C(21)-C(22)	111.7(2)
C(1)-N-C(21)	111.6(2)	C(21)-C(22)-O(23)	117.8(2)
C(11)-N-C(21)	112.9(2)	C(21)-C(22)-O(24)	118.1(2)
N-C(1)-C(2)	115.1(3)	O(23)-C(22)-O(24)	124.1(3)
C(1)-C(2)-C(3)	118.1(2)	Co(2)-O(13)-C(12)	116.4(2)
C(2)-C(3)-O(4)	117.4(2)	Co(2^{i})-O(5)-C(3)	125.3(2)
C(2)-C(3)-O(5)	118.6(2)	Co(2)-O(5)-C(3)	124.7(2)
O(4)-C(3)-O(5)	124.0(2)	Co(2)-O(5)-Co(2^{i})	103.51(8)
N-C(11)-C(12)	110.0(2)	Co(2)-O(23)-C(22)	116.8(2)

[a] Numbers in brackets give the multiplicity. [b] Symmetry code (i): $1-x$, $-y$, $1-z$.

dihedral angles in the analogous ring of the complex [Ni(β-alaninato)$_2$(H$_2$O)$_2$ (−56, 74, −27, −29, 35 and 10°, respectively) [20]. However, it is interesting to note the influences of the unusual monoatomic bridging role of the O(5) atom in the structural parameters of the carboxylate group from the β-alaninate arm. The length of the bonds C(3)–O(4) and C(3)–O(5) of L^{3-} correlates very well with the corresponding average values of the monoatomic bridged acetato groups in copper(II) derivatives (1.227 and 1.274 Å, respectively) [16, 19].

Crystal packing

In addition to the eight water molecules bonded to the cobalt(II) atoms, there are four hydrogen bonded water molecules in the unit cell, namely OW(5)H$_2$ and OW(6)H$_2$, and their symmetry related ones by the inversion center (referred by the superscipt i). Among the twenty four hydrogen atoms of the water molecules in the unit cell, all but two are involved in hydrogen bond formation. These two atoms are H1OW(6) and H1OW(6^{i}). In addition, each of the two water molecules of the dimeric anion can be involved in three of such bonds:

	Distance (Å)	Angle (°)
OW(4)-H1(OW4)···O(4^{iii})	3.015(3)	163
OW(4)-H1(OW4)···O(4^{i})	2.774(3)	116
OW(4)-H2(OW4)···O(24^{iv})	2.684(3)	161

Symmetry codes: (i): $1-x$, $-y$, $1-z$; (iii): $1+x$, y, z; (iv): $1-x$, $-y$, $-z$.

Thus, the atom H1(OW4) seems responsible for a 'bifurcated' hydrogen bond, where the shorter distance and the lower angle correspond to one intramolecular hydrogen bonding interaction, two of which will contribute to the overall stability of the dimeric anion $[Co_2L_2(H_2O)_2]^{2-}$. In summary, the crystal consists of discrete cations $[Co(H_2O)_6]^{2+}$, anions $[Co_2L_2(H_2O)_2]^{2-}$ and water molecules connected together by a network of twenty two hydrogen bonds per unit cell (on average). These bonds and many other van der Waals contacts contribute to the cohesion of the crystal of the title compound. X-ray diffraction data for both title cobalt and zinc compounds lead to the conclusion that their structures are isotype in the light of their very small parameter changes and of their space-group identity.

The cell parameters of the zinc complex are: $a = 8.697(2)$, $b = 9.772(3)$, $c = 9.965(1)$ Å, $\alpha = 100.42(6)$, $\beta = 110.72(5)$, $\gamma = 103.37(2)°$.

Properties of the compounds $[M(H_2O)_6][M_2L_2(H_2O)_2]\cdot 4H_2O$ (M(II) = Co(II), Zn(II))

Thermal stability

The hydrated crystals of both studied compounds are stable at room temperature, but they lose water easily on heating. Both compounds lose the water molecules unbounded to the metal above 380 K (at 327–365 K for the Zn samples and 333–373 K for the Co(II) compound). The loss of coordinated water molecules occurs in overlapped endothermic steps, at 373–440 K for the Co(II) derivative and mainly at 365–410 K for the Zn compound, although this later is anhydrous only at 550 K (total water loss: calc. 26.6%, exp. 26.7%). Greater differences are recorded for the pyrolytic decomposition of the anhydrous M_3L_2 residues. This process occurs for the Zn samples in several overlapped exothermic steps, within a considerable range of temperature (588–725 K) to give a residue of ZnO and $Zn(NO_3)_2$ (calc. 33.3%, exp. 30.2%). In clear contrast, the anhydrous Co_3L_2 decomposes over 558 K with a strong exothermic effect at 570–600 K giving a variable residue (20–40%).

Infrared spectra

In accordance with their isostructural correlations, the solid samples of the compounds $[M(H_2O)_6][M_2L_2(H_2O)_2]\cdot 4H_2O$ (M = Co, Zn) have very similar IR spectra, with broad absorption bands near 3400 and 700 cm^{-1} mainly due to ν(O–H) and deformation modes of the water molecules. In addition, the deformation mode $\delta(H_2O)$ appears as a shoulder (at 1660–1640 cm^{-1}) of an intense absorption, where we can appreciate a shoulder at 1680 cm^{-1} and the strongest band at 1600–1570 cm^{-1}, both due to the antisymmetric stretching mode ν_{as}(COO) of the carboxylate groups. These spectra also show two well defined bands of the corresponding symmetrical stretching mode ν_s(COO), at fairly constant frequencies of 1400 and 1370 cm^{-1}, of which the latter is the weaker one.

In accordance with the structure of the anion $[Co_2L_2(H_2O)_2]^{2-}$ here reported, we should expect less intense absorptions with a large splitting value $\Delta\nu(COO) = \nu_{as}(COO) - \nu_s(COO)$ for the monoatomic bridging carboxylate groups. On this basis, we attribute the shoulder at 1680 cm^{-1} and the band at 1400 cm^{-1} to the stretching modes of the monoatomic bridged carboxylate group, with a value of $\Delta\nu(COO) = 280$ cm^{-1} for both compounds. The mode ν_{as}(COO) of the univalent (non-bridging) carboxylate groups are recorded at 1595 and 1580 cm^{-1} for the cobaltous derivative, and at 1590 and 1575 cm^{-1} for the zinc analogue. These data and the fairly constant frequency of the corresponding mode ν_s(COO) (1370 cm^{-1}) lead to their mean splitting values $\Delta\nu$(COO) of 218 and 213 cm^{-1} for the Co and Zn compounds, respectively. The splitting values $\Delta\nu$(COO) of these spectra correspond to a considerable ionic character for the carboxylate-to-metal bonds in the dimeric anions of both studied compounds. A $\Delta\nu$(COO) value of *c.* 240 cm^{-1} has been reported for the monoatomic acetato bridged groups in a copper(II) complex [19].

Magnetic data

The molar susceptibility was measured at 4.2 and 293 K as well as in the range 35–116 K. Our results show that the paramagnetism of the solid $[Co(H_2O)_6][Co_2L_2(H_2O)_2]\cdot 4H_2O$ has the Curie–Weiss-like behaviour, $\chi = C/(T-\theta)$, with $C = 8.50$ K emu mol^{-1} and $\theta = -10$ K (see 'Supplementary material'). Obviously, the data reflect the average magnetic properties of the Co(II) atom in both complex ions present in the crystal structure, from which we obtained an average magnetic moment of $\mu = 4.9\mu_B$ per mole of Co(II) atoms. No evidence of antiferromagnetic interaction has been obtained. At very low temperatures, a weak antiferromagnetic exchange interaction has been reported for dinuclear Cu(II) complexes with the 'Cu_2O_2' unit involving monoatomic acetate bridges, having Cu–O–Cu angles of 98.3 and 95.3° [18, 19]. The angle Co–O–Co^i (103.5°) of the Co_2O_2 bridging unit in the studied compound can be too open, but this suggestion should be clarified by the study of analogous compounds where the hexaaquacobalt(II) cation could be replaced by a diamagnetic counter-cation. The synthesis of this kind of analogous compound is in progress.

Supplementary material

Tables giving thermal motion factors, atomic coordinates and isotropic thermal parameters of hydrogen atoms, least-squares mean plane equations, torsion angles, C–H and O–H bond lengths (Å), hydrogen bond distances (Å) and angles, and van der Waals distances less than 3.60 Å; Fig. 2 showing the stereoscopic view of the cell; Figs. 3–5 showing the TG and DTA diagrams of $[Cl(H_2O)_6][Co_2L_2(H_2O)_2]\cdot 4H_2O$ and $[Zn(H_2O)_6][Zn_2L_2(H_2O)_2]\cdot 4H_2O$, and the IR spectra of both compounds, respectively; Fig. 6 showing a plot of inverse molar susceptibilities of $[Co(H_2O)_6][Co_2L_2(H_2O)_2]\cdot 4H_2O$ versus temperature; and a listing of observed and calculated structure factors are available from the authors on request.

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